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(U) CATALYTIC REACTIONS OF DISSOCIATION PRODUCTS
OF AMMONIUM PERCHLORATE *†

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In a recent publication¹ we presented some experimental results on the thermal decomposition of solid ammonium perchlorate (AP) at elevated temperatures ($T > 525^\circ\text{K}$) and the catalytic effects associated with the addition of copper chromite. It was observed that the activity of the catalyst in contact with AP is gradually destroyed as the reaction proceeds. This change in catalytic properties was associated with a change in the oxidation state of the chromium cation from Cr(III) in copper chromite, CuCr_2O_4 to Cr(VI) . However, on the basis of the experiments we were unable to distinguish whether the original dissociation products of ammonium perchlorate², NH_3 and HClO_4 , or the intermediates resulting from the catalyzed reaction act as the oxidizing agent for the catalyst. In addition, the role of gas-phase reactions and surface-coupled reactions requires further elucidation so that the mechanism of decomposition of solid propellants based on AP may be better understood.

In order to examine in more detail the catalytic processes involving gaseous ammonia and perchloric acid, a series of experiments was carried out in which the sublimation products of AP were employed as a source of reactants. The catalyst, copper chromite, was exposed to these gaseous reactants, rather than placed in immediate contact with the solid AP. A similar experiment with nickel oxide has been reported recently.³

A cylindrical reactor was constructed which contained a pressed pellet of AP (2.5 cm in diameter, 1.5 cm in height) over which a stream of helium was passed (volumetric flow rate of 160 cc/min). The catalyst (Harshaw Cu-0202p) was enclosed in a thin-walled glass bulb and placed in a shallow well approximately 2.5 cm on the downstream side of the AP pellet. Prior to an experiment the air in the void volume of the glass bulb was displaced by helium at 1 atmosphere. The entire reactor was surrounded by a electric furnace whose temperature was controlled at 675°K . The sample was heated at this temperature while the helium gas passed over it and carried away the gaseous products through a bed of moistened sodium hydroxide pellets (to remove Cl_2 , HCl , and HNO_3). The

composition of the remaining gas mixture (O_2 , N_2 , and N_2O) was analyzed at suitable time intervals by gas chromatographic techniques. A column packed with Poropak Q* and operated at $350^\circ K$ was employed to separate N_2O from O_2 and N_2 , while a column packed with molecular sieve** allowed adequate separation of N_2 from O_2 .

In order to reduce the concentration of decomposition products, the AP pellet was heated at $675^\circ K$ for more than 30 minutes. This length of time was sufficient to ensure the disappearance of the "intermosaic" material⁴ from the AP. After this period the distribution of the three products (N_2 , O_2 , N_2O) issuing from the reactor was analyzed (Figure 1). Ammonia and perchloric acid formed by the dissociative sublimation of AP condensed in the cool, downstream portion of the apparatus, a considerable distance from the catalyst.

By shattering the bulb containing the catalyst, the gaseous reactants, NH_3 and $HClO_4$, were allowed to come in contact with the copper chromite powder. The change in product distribution resulting from the heterogeneous reaction can be seen from the data in Figure 1. It will be noted that of the gaseous products analyzed, the concentration of oxygen exhibits a marked increase as the result of the catalytic reaction. To a lesser extent the partial pressures of N_2O and N_2 show a positive change. Within a few minutes, however, the effluent gas mixture returns to its original composition. It is apparent that the catalytic properties of copper chromite are altered materially on exposure to the dissociation products of AP, similar to the observations made previously¹ where the catalyst was admixed to the solid AP. The cause of the loss in catalytic activity was associated with oxidation of Cr(III) in the copper chromite to the higher oxidation state Cr(VI).

The observed increase in oxygen concentration preceding the catalyst modification (Figure 1) suggests that the original catalyst affects the decomposition of $HClO_4$ and not the reactions of ammonia or of ammonia and perchloric acid. In a recent publication⁵ the catalytic

* Dow Chemical Company.

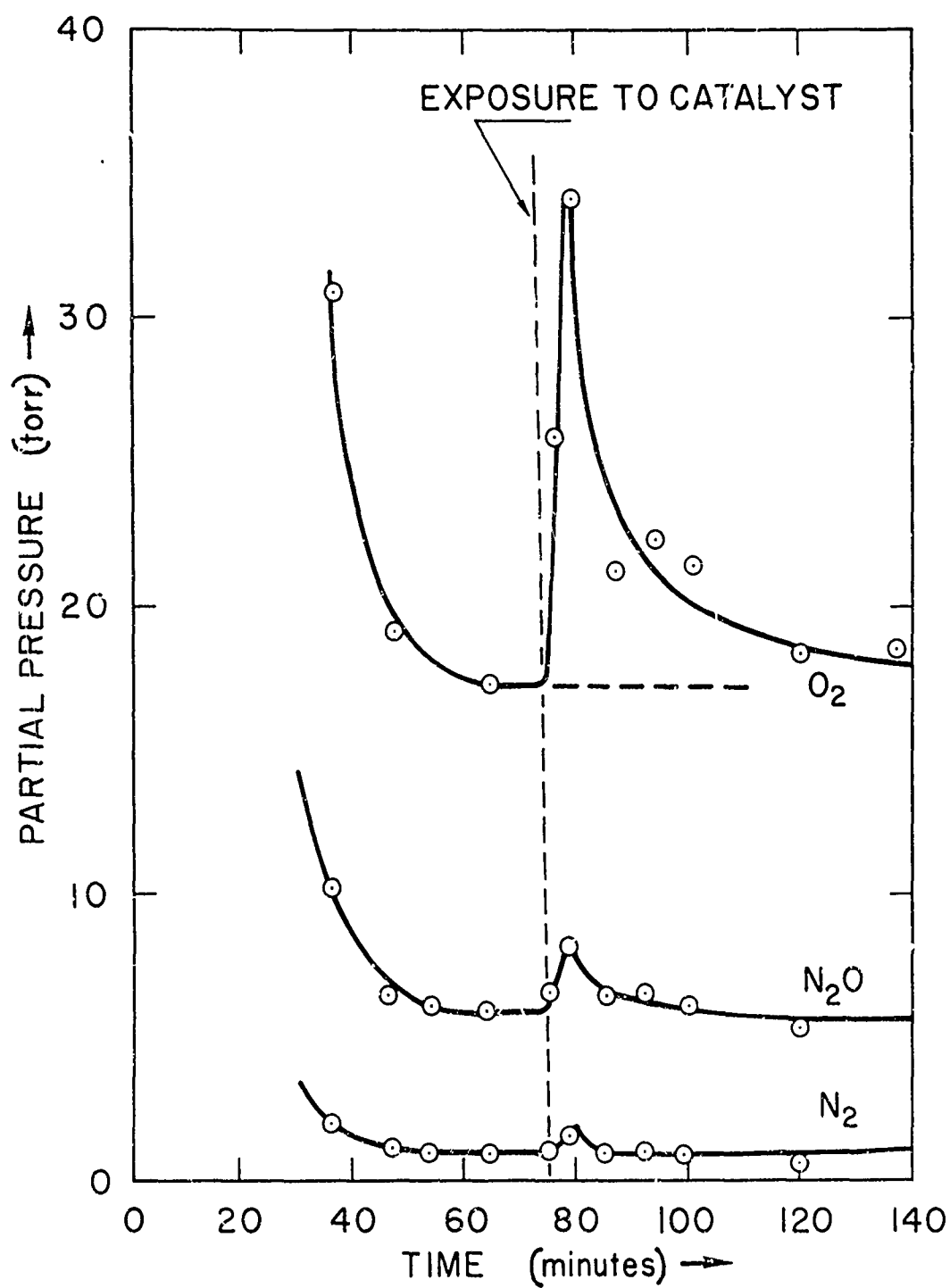
** Linde Molecular Sieve (5 \AA).

decomposition of perchloric acid vapor diluted with nitrogen was investigated in the presence of chromic oxide. At temperatures above 575°K a loss in catalytic activity of the Cr_2O_3 was noted on prolonged exposure to HClO_4 , similar to our observations with copper chromite.

In a solid propellant containing AP and binder, the action of a catalyst such as copper chromite may be sustained by the presence of the organic molecules present in the binder. Undoubtedly their reactions with various oxidizing agents on the catalytic surface will prevent changes in the oxidation state of the chromium or result in an oxidation-reduction cycle. Apparently the surface-catalyzed kinetics of ammonia oxidation at the concentrations employed in our systems with a carrier stream are unfavorable for such a process of maintaining Cr(III) at the catalytic surface. Since a very rapid self-sustaining reaction occurs at 675°K with complete consumption of AP when the catalyst is admixed to the AP, we must conclude that under these conditions the rates of catalytic reactions involving NH_3 are rapid enough to allow a redox cycle of the catalyst. In related experiments⁶ on the reaction with oxygen of a representative organic binder molecule, such as propylene, the copper chromite catalyst was found to be most effective in complete oxidation of propylene to CO_2 and H_2O (at 625°K) without any loss in activity over long periods of time. Most likely the copper chromite catalyst, a spinel structure of $\text{CuO} \cdot \text{Cr}_2\text{O}_3$, plays a dual role in propellant kinetics: a) an oxidation catalyst for ammonia and organic binder molecules, and b) a decomposition catalyst for perchloric acid. While the oxidation process appears to be unaffected by changes in the chromium cation valence state (perhaps copper cation is the important partner), the decomposition reaction of perchloric acid seems to be sensitive to the valence state of chromium.

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<p>An experimental study of the decomposition kinetics of ammonium perchlorate (AP) demonstrated that the action of the catalyst copper chromite in contact with solid AP differs markedly from that of the catalyst in contact with the gaseous dissociation products of AP. On exposure to ammonia and perchloric acid at 675°K the catalyst loses rapidly its activity. A process which appears to be due to the oxidation of chromium cation from the +3 to a higher oxidation state.</p>		